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PRODUCTION OF PIGMENTS BASED ON COBALT ZIRCONATE USING THE PRECIPITATION METHOD

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Ceramic pigments based on cobalt zirconate were obtained using the precipitation method. The IR absorption spectra support the possibility of cobalt zirconate formation at the precipitation stage. The color characteristics of the pigments suggested for tinting glass and ceramics are presented.

The most stable coloring agent for ceramic mixtures and glazes is cobalt. Cobalt oxide can impart color by acting as a pigment (in the bonded crystalline state), or in accordance with the ion coloring principle. In the latter case, the tint of CoO and other oxides depends on their coordination number (CN). If the coordination number of CoO is equal to 6, it will act as a modifier in the glass structural net, and its color tone will be purple. If it acts as a net-former, its coordination number is 4, and it imparts a blue color.

The coordination number for the cobalt-containing pigments is determined by the crystal lattice on the basis of which the pigment is synthesized and in which Co^{2+} ions are incorporated. The pigment in glaze melts is partly dissolved, which leads to the modification of its color and coordination number.

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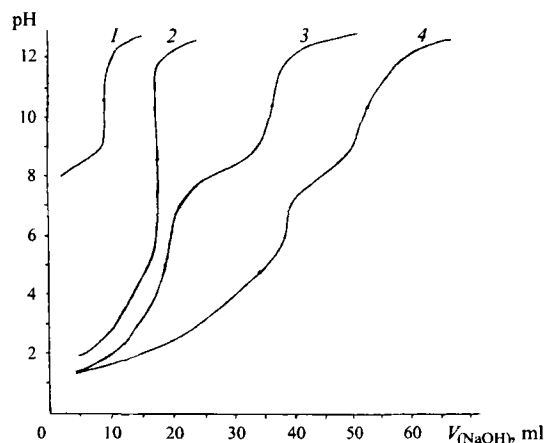


Fig. 1. Potentiometric titration curves of solutions: 1) cobalt(II); 2) zirconium(IV); 3) cobalt(II) – zirconium(IV) in the ratio of 1 : 4; 4) cobalt(II) – zirconium(IV) in the ratio of 1 : 2.

The purpose of the present investigation was to study the possibility of producing pigments of the perovskite-type structure based on the $\text{CoO} - \text{ZrO}_2$ system by the alkaline precipitation method. The pigments were synthesized from 0.5 M solutions of $\text{Co}(\text{NO}_3)_2$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, and the precipitator was 1 M solution of NaOH. Solid ZrO_2 was used in the synthesis of some samples. The synthesis and the analysis of the pigments were carried out in the same manner as in the earlier studies [1].

Curves (V-74 universal ionometer) of alkali titration of the solution are shown in Fig. 1. Their analysis makes it possible to conclude that the precipitated Co(II) and Zr(IV) ions have a mutual effect on each other's hydrolytic properties until the moment of solid phase formation. The pH of the combined precipitate is lower than the pH of precipitated cobalt and zirconium hydroxides. Two jumps should be observed in titration curves 3 and 4 corresponding to the consecutive precipitation of Zr(IV) and Co(II) hydroxides, which is indeed the case. However, the shape of the curves suggests that the precipitate is not a mechanical mixture of the hydroxides.

The IR spectra (UR-20) of the obtained precipitates (Fig. 2) exhibit absorption bands due to the valence vibrations of water molecules and OH groups within the range of $2800 - 3700 \text{ cm}^{-1}$, deformation vibrations of H_2O molecules ($1617 - 1632 \text{ cm}^{-1}$), and valence vibrations of the Me-O bond ($400 - 700 \text{ cm}^{-1}$) [2]. The high intensity of these bands points to a substantial content of nonstructural water in the precipitates.

The deformation vibration band of OH-groups in the region of $1047 - 1073 \text{ cm}^{-1}$ [2] was not identified in the precipitate spectra Co : Zr = 1 : 1 and Co : Zr = 1 : 2 (reverse sequence of pouring). This suggests that alkaline precipitation did not produce hydroxide precipitates but rather salts, namely, zirconates. Within the spectrum of the precipitate Co : Zr = 1 : 2 (direct pouring) this band is manifested at

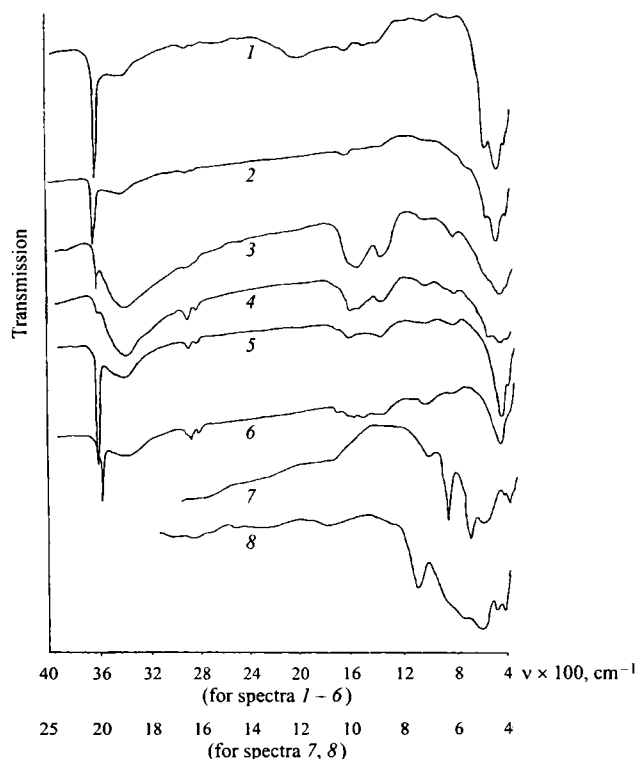


Fig. 2. IR absorption spectra: 1) cobalt hydroxide; 2) precipitate $\text{Co}:\text{Zr} = 1:1$; 3) precipitate $\text{Co}:\text{Zr} = 1:2$, direct sequence of pouring; 4) the same, reverse sequence of pouring; 5) precipitate $\text{Co}:\text{Zr} = 4:1$, direct sequence of pouring; 6) the same, reverse sequence of pouring; 7) calcined precipitate $\text{Co}:\text{Zr} = 1:1$; 8) calcined zirconium hydroxide.

$1050 - 1073 \text{ cm}^{-1}$, but its intensity is negligibly low, which is evidence of the presence of hydroxide impurities. Within the spectra of the precipitates $\text{Co}:\text{Zr} = 4:1$ produced by direct and reverse pouring, this band is manifested with medium intensity at 1060 and $1023 - 1065 \text{ cm}^{-1}$. Presumably, apart from cobalt zirconate, cobalt hydroxide is also precipitated in such systems under the effect of the alkali, since Co(II) is taken in excess.

Within the Co(OH)_2 spectrum, the deformation vibrations of OH groups are manifested in the form of a weak band of medium intensity at 1035 cm^{-1} . The most significant differences between the Co(OH)_2 spectrum and the spectra of the precipitates $\text{Co(II)} - \text{Zr(IV)}$ are registered in the region of 2015 , $1495 - 1630$, and $745 - 1035 \text{ cm}^{-1}$.

The spectra of the precipitates with the molar ratios $\text{Co}:\text{Zr} = 1:2$ and $4:1$ obtained by a different pouring sequence significantly differs from each other and from the spectrum $\text{Co}:\text{Zr} = 1:1$. The most perceptible differences are found within the range of the valence vibration region of the Me-O bond at $400 - 700 \text{ cm}^{-1}$.

In the case of excess of zirconium, the narrow band at $3622 - 3627 \text{ cm}^{-1}$ typical of the Co(OH)_2 spectrum significantly decreases (if the precipitate was obtained by direct

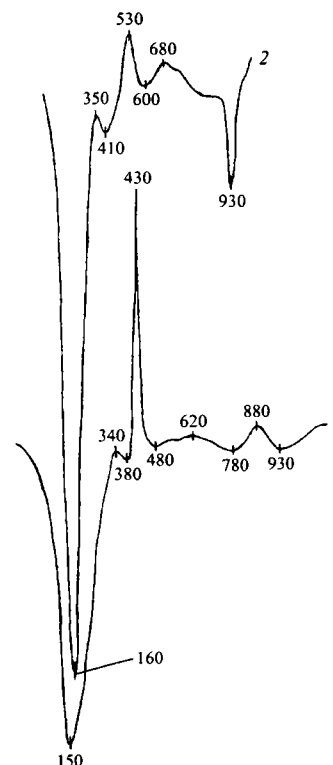


Fig. 3. DTA curves: 1) zirconium hydroxide; 2) precipitate $\text{Co}:\text{Zr} = 1:1$.

pouring), or almost disappears (reverse pouring). This band which is preserved as well in the spectrum of the precipitate $\text{Co}:\text{Zr} = 1:1$, in this case is presumably superimposed by a very wide and intense band of H_2O valence vibrations in zirconium hydroxide, which was formed due to the excess of Zr(IV) in the system.

Owing to the presence of the second phase, a wide, intense, double band appeared in these spectra at $1382 - 1620 \text{ cm}^{-1}$. The band with three maxima within the region of $400 - 700 \text{ cm}^{-1}$ typical of Co(OH)_2 and CoZrO_3 is distorted due to the superimposition of the bands of valence vibrations of the Zr-O bonds in zirconium hydroxide.

If cobalt is taken in 4-fold excess with respect to zirconium, the bands at 2015 and 1495 cm^{-1} typical of Co(OH)_2 are absent in the spectra of these precipitates and in the CoZrO_3 spectrum as well. However, as distinct from CoZrO_3 , the Co(OH)_2 bands at $912 - 920$ and $845 - 855 \text{ cm}^{-1}$ are preserved within the specified spectra. The intense bands within the range of the Me-O bond vibration at $442 - 500 \text{ cm}^{-1}$, which were observed in the spectra of Co(OH)_2 and CoZrO_3 , are slightly distorted, but nevertheless are present.

Thus, it can be assumed that with a nonstoichiometric molar ratio of $\text{Co}:\text{Zr}$, the products are CoZrO_3 and the hydroxide of the metal which is taken in excess. Judging from the fact that the spectra of the precipitates $\text{Co}:\text{Zr} = 4:1$ are not additive to the spectra of Co(OH)_2 and CoZrO_3 , we can-

not rule out the formation of other phases in these systems, for instance, the basic cobalt zirconates. Moreover, it should be noted that the sequence of pouring the solutions has a significant effect on the precipitate composition.

The IR spectra of the precipitate of zirconium hydroxide and Co(II)-Zr(IV) roasted to temperatures of 1000 and 1200°C, respectively, were obtained as well (Fig. 2, curves 7, 8). All bands in them are within the range of 420–1186 cm^{-1} , and the highest intensity is exhibited by the vibration bands of the Me–O bond. On the one hand, the spectrum of Co(II)–Zr(IV) has a simpler outlook than the spectrum of the same precipitate without calcination, due to the absence of the absorption bands of H_2O molecules and OH groups. On the other hand, the data of the IR-spectroscopy corroborate the transition of the sample from the amorphous to the crystalline state in the course of calcination, as a consequence of which the spectrum (Fig. 2, curve 8) within the vibration range of the Me–O bond has more absorption bands. The intensity of these bands is higher than in the case of the nonroasted precipitate.

Comparing the absorption band frequencies, the following observations can be made. The IR spectrum of the calcined precipitate does not have the absorption bands of ZrO_2 . Therefore, the sample does not contain individual ZrO_2 . Only one band at 582 cm^{-1} within this spectrum virtually coincides with one of the bands of the Co(OH)_2 spectrum at 585 cm^{-1} , which makes it possible to attribute it to the vibrations of the Co–O bond. Consequently, individual CoO is absent in the sample as well. Based on the data in [3], the bands at 427, 532, and 582 cm^{-1} can be attributed to $\nu(\text{ZrO})$ vibrations. The bands at 668 and 740 cm^{-1} do not relate to CoO and ZrO and probably relate to the vibrations of the bonds Co–O–Zr in the newly formed compound. Since the position of the absorption bands corresponding to the bonds Co–O and Zr–O in the sample of Co(II)–Zr(IV) changes significantly, this means that the new bond Co–O–Zr becomes the dominant one.

The thermogram of zirconium hydroxide (Fig. 3) registers the endothermic effects of dehydration and the exothermic effect. Virtually all water is removed up to a temperature of 380°C, and the total weight loss is 26%. The DTA curve registers an exothermic effect related to the formation of the crystalline precipitate of the monoclinic modification, which at a temperature of 880°C converts to the tetragonal modification, which is evidenced by the exothermic effect. Since the structure of the precipitate is somewhat weakened, the polymorphic transformations occur at a lower temperature,

as compared to the temperature of the initial crystalline ZnO. The reversible character of the modification transformations leads to compression, expansion, and cracking of the articles made of ZrO_2 . The introduction of CoO stabilizes and strengthens the crystal lattice, due to the formation of substitutional solid solutions, which should prevent the transition of the unstable high-temperature modification of ZrO_2 to the monoclinic one.

With the ratio Co:Zr = 1:1 in the sample, the DTA curve shows the loss of 70% H_2O at the temperature of 160°C. The exothermic effect is observed at 530°C, i.e., at a higher temperature than in the case of zirconium hydroxide. The exothermic effect is significantly less intense. The deep endothermic effect at the temperature of 930°C is determined by the formation of cobalt zirconate.

The obtained pigments are characterized by the wide absorption bands in the medium range of the spectrum. The formation of the color-bearing phase is completed at a temperature of 1000°C, and it is represented by $[\text{CoO}_4]$ which is more thermodynamically stable in the vitreous silicate phase and acts through the ion tinting mechanism. The dominant wavelength is 469 nm, and the dominant color is bright blue. The color can be slightly modified in the case of introduction of Na_2SiO_4 to the composition containing ZrO_2 :CoO in the ratio of 1:1. In this case, the quantity of $[\text{CoO}_6]$ slightly increases. The pigment compositions containing SiO_4 produce Co_2SiO_4 of orthorhombic syngony, in which cobalt has the predominantly octahedral environment. The pigments exhibit high brightness and resistance to the dissolving effect of fluxes and glazes.

Thus, the temperature of the synthesis of pigments obtained by the precipitation method was 100–200°C lower compared to the pigments synthesized from powders. Moreover, preliminary fine milling is not required in this case, which allows for significant savings in energy consumption and elimination of the milling bodies. The resulting pigments are purer and brighter and can be recommended for flux and glaze tinting.

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